1,3-Diphenyl-1,3-dichloro-2,2-dimethylhydrindene (VI).—A solution of 1 g. of the diaddition compound II in anhydrous benzene was saturated with dry hydrogen chloride. A few grains of anhydrous calcium chloride were present to remove water formed in the reaction. After removal of the benzene the product was crystallized from ligroin. It melted at 177–178°.

Anal. Calcd. for $C_{23}H_{20}Cl_2$: C, 75.20; H, 5.49; Cl, 19.31. Found: C, 75.09; H, 5.32; Cl, 19.33.

Treatment of this compound with boiling methanol converted into the oxido compound VIII, m. p. 70°.

Attempts to Cleave the Monoaddition Compounds I.—1. To a solution of 8 g. of 1,3-diketo-2,2-dimethylhydrindene in anhydrous benzene was added over three hours an ether solution of 0.025 mole of phenylmagnesium bromide. The ether was removed by distillation until the boiling point of the solution reached 80°. The solution was refluxed for sixteen hours. At the end of this time an excess of phenylmagnesium bromide was added and the diaddition product isolated as described above. There was obtained a 79% yield of II. While this does not represent a quantitative recovery, the isolation of pure material from the last residues of the product in crystallization mother liquors was difficult. No evidence for the presence of any other compound could be obtained.

2. To a solution of 2.60 g. of the monoaddition compound (I) in 100 ml. of anhydrous isopropyl ether was added a carefully measured amount of phenylmagnesium bromide in ether corresponding to exactly one mole of reagent. A white precipitate formed during addition of the reagent. The ethyl ether was removed and the solution refluxed at the boiling point of isopropyl ether for sixteen hours. Upon working up the reaction mixture the starting material was recovered unchanged. No other product could be found. The yield of recovered product was, after recrystallization, only about 70% but this corresponds to experience in isolating and purifying the substance in other experiments. The formation of a small amount of the diaddition compound (II) during the addition of the reagent to the monoaddition compound could easily account for the poor recovery, since the presence of an amount of the diaddition compound too small for isolation would undoubtedly, in view of its similarity in solubility and crystallizing tendency, make it difficult to induce all of the other substance to crystallize. For example, Weiss and Luft[5] were able to obtain only a 20% yield of I from what has been shown in this work to be a mixture of I and II.

Summary

1. The reaction of 1,3-diketo-2,2-dimethylhydrindene with phenylmagnesium bromide has been studied and it has been found that normal addition of either one or two moles of the reagent to the carbonyl groups of the diketone occurs. No evidence for cleavage was obtained.

2. The results have been discussed in their relation to the reaction of straight-chain β-diketones with Grignard reagents, where cleavage of the molecule can be brought about.

LOS ANGELES, CALIFORNIA RECEIVED JULY 28, 1941

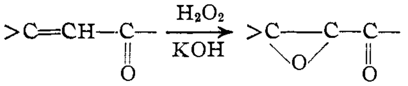
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Osage Orange Pigments. VIII.[1] Oxidation

BY M. L. WOLFROM AND A. S. GREGORY

In a previous communication[2] from this Laboratory, it was shown that osajin dimethyl ether yielded anisic (*p*-methoxybenzoic) acid on oxidation with alkaline hydrogen peroxide and that pomiferin trimethyl ether yielded veratric (3,4-dimethoxybenzoic) acid under the same conditions. It is now shown that the oxidation of pomiferin trimethyl ether (I) proceeds through the intermediate formation of a ketoxide (II), isolatable in high yield, and designated pomiferin trimethyl ether 2,3-epoxide. Such an intermediate was not isolatable in the oxidation of osajin dimethyl ether, but there is no reason to believe that the reaction does not follow a similar course. A ketoxide of iso-osajin was obtained. The expected entity III apparently underwent extensive destruction under the oxidizing conditions and was not isolated.

Weitz[3] found that α,β-unsaturated ketones reacted with hydrogen peroxide in the presence of low alkalinity to form compounds designated ketoxides which differed from the initial ketone by the addition of one atom of oxygen to the molecule and liberated iodine in the hot, but not in the cold, from an acetic acid solution of potassium iodide. The structures of these substances were established definitely.[4] Such ketoxides were not isolatable in all cases, further oxidation being at times more rapid than their formation.



$$>C{=}CH{-}\underset{\underset{O}{\|}}{C}{-}\xrightarrow[KOH]{H_2O_2}>\underbrace{C{-}{-}C}_{O}{-}\underset{\underset{O}{\|}}{C}{-}$$

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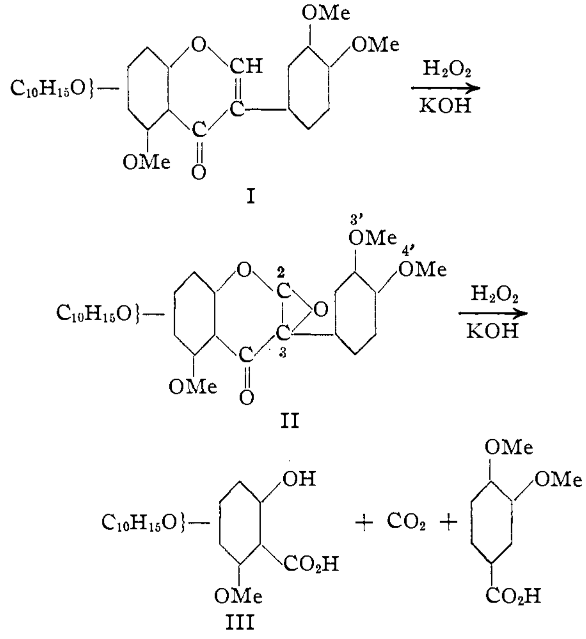
(1) Preceding publication in this series, M. L. Wolfrom and J. E. Mahan, THIS JOURNAL, **63**, 1253 (1941).

(2) M. L. Wolfrom and A. S. Gregory, *ibid.*, **62**, 651 (1940).

(3) E. Weitz, *Ann.*, **418**, 34 (1919).

(4) E. Weitz and A. Scheffer, *Ber.*, **54B**, 2327 (1921).

The assignment of ketoxide structures to the oxidation products herein described is based upon their method of formation, analysis, behavior toward potassium iodide–acetic acid, and to their further oxidizability. The formation of these substances is therefore additional confirmation of our assignment of the isoflavone structure[1,5] to osajin and pomiferin, since an α,β-ketonic linkage is present in the isoflavone nucleus. To our knowledge, ketoxide formation has not hitherto been observed in the isoflavone series. The formation of a ketoxide from tetrahydropomiferin is further proof that neither of the two double bonds reduced in that substance is involved in the isoflavone nucleus.



In a previous communication[6] we have presented evidence to show that in the acid isomerization of osajin and pomiferin, a double bond and a phenolic group disappear, presumably by addition of the phenolic group to the double bond to form a cyclic ether. We can now report that iso-osajin and isopomiferin yield ketoxides on oxidation with alkaline hydrogen peroxide and on further oxidation with the same oxidant yield, respectively, anisic and veratric acids. These facts may then be presented as proof that neither the double bond between carbon atoms two and three nor the phenolic groups substituted in the phenyl substituent on carbon three, is involved in this isomerization. The partially methylated ethers of osajin and pomiferin can be isomerized[6] and it then may be inferred that the phenolic groups methylated in these substances are those on the phenyl substituent on carbon three. The allocation of these methoxyl groups is now established by the oxidation, herein reported, of pomiferin dimethyl ether and of osajin momomethyl ether to veratric and anisic acids, respectively.

Experimental

Synthesis of 2,3-Epoxides.—Pomiferin trimethyl ether (2 g.), dissolved in 100 cc. of acetone, was treated with 20 cc. of 30% hydrogen peroxide and 2 cc. of 5% potassium hydroxide. Stirring was maintained for twelve hours, at which time fine white crystals were removed by filtration; yield 1.2 g., m. p.[7] 159.5°. The compound could be recrystallized from acetone–water or from benzene–petroleum ether but remained unchanged in melting point. A further quantity (0.4 g., m. p. 148–149°) could be obtained by room temperature concentration of the mother liquor to half volume and recrystallization of the separated material.

The other 2,3-epoxide derivatives recorded in Table I were prepared in the above-described manner with some variations in the time of reaction, as noted. Purification could be effected from the same solvents. The yields recorded (for those other than pomiferin trimethyl ether 2,3-epoxide) are based upon the amount of the first crop isolated after the stated time interval and are not the maximum obtainable. No 2,3-epoxide formed in the case of osajin dimethyl ether.

All of the derivatives listed in Table I liberated iodine from a solution of potassium iodide in glacial acetic acid on boiling but not at room temperature (over an observation period of thirty minutes). This is a test cited by Weitz and Scheffer[4] as characteristic of ketoxides.

Veratric and Anisic Acids.—Pomiferin trimethyl ether 2,3-epoxide (II), tetrahydropomiferin trimethyl ether (IV), isopomiferin trimethyl ether (V) and pomiferin dimethyl ether were each oxidized in acetone solution with alkaline hydrogen peroxide according to the procedure described in a previous publication.[2] These oxidation conditions differed from those used in preparing the epoxides in that more acetone, a longer time, and a higher concentration of alkali were employed. In the oxidation of V, the 2,3-epoxide separated from the reaction mixture but redissolved slowly on further reaction. The ether-soluble acid fractions of the final oxidation mixtures were in all cases isolated and purified in essentially the same manner as described in our previous publication.[2] The purified acid was identified in all cases as veratric acid (m. p. 179–180°, mixed m. p. unchanged). The yield obtained was approximately 0.2 g. of veratric acid from 1.7 g. of starting product except that in the case of V a lower yield was isolated (30 mg. of veratric acid from 1 g. of V). The same oxidation conditions (long time, more acetone, and higher alkali concentration) were applied to iso-osajin mono-

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(5) M. L. Wolfrom, J. E. Mahan, P. W. Morgan and G. F. Johnson, THIS JOURNAL, 63, 1248 (1941).

(6) M. L. Wolfrom, F. L. Benton, A. S. Gregory, W. W. Hess, J. E. Mahan and P. W. Morgan, *ibid.*, 63, 422 (1941).

(7) All melting points are uncorrected.

TABLE I

2,3-EPOXIDES OF OSAJIN AND POMIFERIN DERIVATIVES

Substance, 2,3-epoxide	Time of reaction, hours	Yield, %	M. p., °C.	Calcd. C	Calcd. H	Calcd. OMe	Calcd. Mol. wt.	Found C	Found H	Found OMe	Found Mol. wt. (Rast)
Pomiferin trimethyl ether	12	80	159.5	70.27	6.32	19.46	478.5	70.13	6.32	19.48	441
Tetrahydropomiferin trimethyl ether	16	10	150–151	69.69	7.10	19.29		69.77	7.00	19.1	
Isopomiferin dimethyl ether	3	82	200[a]	69.81	6.08	13.36		69.90	6.08	13.0	
Iso-osajin monomethyl ether	5	63	199.5–200[a]	71.87	6.03	7.14		72.21	6.04	7.16	

[a] Mixed m. p. 180–185°.

methyl ether and produced, with initial separation of the 2,3-epoxide, anisic acid (m. p. 180°, mixed m. p. unchanged) in a yield of 0.5 g. from 1.7 g. of starting material. Likewise, osajin monomethyl ether yielded anisic acid (m. p. 180°, mixed m. p. unchanged) in a yield of 0.3 g. from 1.7 g. of substance oxidized.

We are indebted to Messrs. Joseph Tracht and Bernard Wilde (N. Y. A. Project O. S. U. 181) for assistance in the laboratory.

Summary

1. The 2,3-epoxides (ketoxides) of pomiferin trimethyl ether, tetrahydropomiferin trimethyl ether, isopomiferin dimethyl ether and iso-osajin monomethyl ether have been prepared.

2. Pomiferin trimethyl ether 2,3-epoxide produces veratric acid on further oxidation.

3. Isopomiferin dimethyl ether and iso-osajin monomethyl ether produce veratric and anisic acids, respectively, on oxidation.

4. Pomiferin dimethyl ether and osajin monomethyl ether produce veratric and anisic acids, respectively, on oxidation.

5. The above facts (1) are in harmony with the previous assignment of an isoflavone structure to osajin and pomiferin; (2) show that the isoflavone nucleus is not reduced in tetrahydropomiferin; (3) prove that neither the isoflavone double bond (2, 3) nor the side chain hydroxyls (4′ in osajin and 3′,4′ in pomiferin) is involved in the acid isomerization characteristic of these pigments; and (4) allocate the methoxyl groups in pomiferin dimethyl ether and osajin monomethyl ether to the 3′,4′ positions for the former and to the 4′ position for the latter.

COLUMBUS, OHIO RECEIVED SEPTEMBER 20, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE GEORGIA SCHOOL OF TECHNOLOGY]

Chlorination of Propyl Trichloroacetates

BY C. W. GAYLER[1] AND HOWARD M. WADDLE

The work of Waddle and Adkins[2] on the chlorination of the butyl esters of trichloroacetic acid and the work of Maxwell[3] on the chlorination of *n*-propyl and *i*-propyl trichloroacetates led the authors to a further study of the chlorination of the propyl trichloroacetates.

By the chlorination of *n*-propyl trichloroacetate and the subsequent rectification of the products, Maxwell[3] isolated a fraction thought to be α-chloro-*n*-propyl trichloroacetate. Due to the inconclusive results, it was thought best to repeat this early work. Also work by Waddle and Adkins[2] revealed no such stable α-chloro substituted product in chlorinated *n*-butyl *s*-butyl, and *i*-butyl trichloroacetates.

Preparation of Esters.—The esters were prepared by refluxing two moles of trichloroacetic acid, Merck U. S. P., with four moles of the alcohol for a period of four hours. The excess alcohol was removed by distillation. The residue was washed successively with 10% sodium carbonate solution and water, dried over solid calcium chloride, and distilled under reduced pressure. The yields obtained were roughly 57% of the theoretical.

Chlorination of Esters.—The esters were chlorinated in the presence of the light from a 150-watt unfrosted bulb at 120° in a manner identical with that described by Waddle and Adkins.[2] Chlorine was passed into the esters until the gain in weight corresponded to monosubstitution, a 34.5-g. increase for each molecular weight of ester chlorinated. The chlorinated esters were fractionated, using a total reflux, partial take-off, packed column. The apparatus and technique used are described by Waddle and Adkins.[2]

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[1] This work was presented for the degree of Master of Science in Chemistry at the Georgia School of Technology by Mr. Gayler, whose present address is University of Texas, Austin, Texas.

[2] Howard M. Waddle and Homer Adkins, THIS JOURNAL, **61**, 3361 (1939).

[3] T. A. Maxwell, Senior Thesis, Georgia School of Technology, 1933.